ISTRAŽIVANJE POVEĆANJA VATROOTPORNOSTI MATERIJALA PRIMJENOM MODERNOG POSTUPKA NANOŠENJA METALNIH PREVLAKA

RESEARCH OF THE INCREASE IN FIRE RESISTANCE OF MATERIALS BY APPLYING A METALLIC COATING USING MODERN METHOD PROCEDURE

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REZIME

U radu je opisano mikrostrukturno ispitivanje spoja osnovnog materijala, austenitnog nehrđajućeg čelika s intermetalnim ojačavanjem klasificiranim prema kemijskom sastavu i osobinama prema standardu SAE AMS 5528 i metalne prevlake označene kao NiCrAlY 4516 prema katalogu proizvođača Sulzer Metco. Prevlaka se nanosi pomoću procesa HVOF postupkom Diamond Jet. Osnovni materijal zajedno s nanesenom prevlakom namijenjen je za rad na povišenim temperaturama. Ispitivanjem pomoću optičke i skenirajuće elektronske mikroskopije utvrđeno je, da je na granicama prisutan aluminijev oksid sa udjelom itrijevog oksida koji ima značajnu ulogu u sprječavanju oksidacije osnovnog materijala na visokim temperaturama. Na granici spoja također su analizirane i promjene u koncentracijama sadržaja legirajućih elemenata.

Original scientific paper

SUMMARY

The paper describes the microstructural examination of a joint of the base material, austenitic stainless steel with intermetallic strengthening classified according to its chemical composition and properties according to standard SAE AMS 5528 and metallic coating marked as NiCrAlY 4516 according to manufacturer catalog, Sulzer Metco. Coating is applied using HVOF Diamond Jet procedure. Basic material together with applied coating is designed to operate at elevated temperatures. By testing with optical and scanning electron microscopy, it was found that at the joint is present aluminium oxide with the presence of yttrium oxide, which play a significant role in the prevention of high-temperature oxidation of the base material. At the joint are also analyzed and the concentration changes in the content of alloying elements.

1. UVOD

Cilj istraživanja je poboljšanje osobina austenitnog nehrđajućeg čelika sa intermetalnim ojačavanjem SAE AMS 5528, nanošenjem metalne prevlake NiCrAlY metodom HVOF, postupkom Diamond Jet [1]. Ovaj materijal (u tekstu legura AMS 5528), se koristi za izradu dijelova turbopunjača automobilskih motora koji rade na temperaturi od 720ºC. U radu je prezentirano ispitivanje strukture u zoni spajanja prevlake i legure. Metalna prevlaka NiCrAlY (u tekstu prevlaka NiCrAlY) nanesena na leguru AMS 5528, sastavljena je od rastopljenih i djelomično rastopljenih čestica, oksida, pora, i razbijenih čestica (krhotina).

1. INTRODUCTION

This paper describes a study of improving the properties of austenitic stainless steel with intermetallic strengthening SAE AMS 5528, by applying a metallic coating using HVOF NiCrAlY method, by Diamond Jet procedure [1]. This material (in the text alloy), is used for making parts of turbochargers car engines that operate at temperatures of 720ºC. It also presents testing of the structure of the zone in which are coatings and alloys jointed. Metal coating NiCrAlY (in the text coating) applied to the alloy, is composed of molten and partly molten particles, oxides, pores, and broken particles (debris).

Struktura legure AMS 5528 u ojačanom stanju se sastoji od austenitne □-osnove, sa koherentno izdvojenom □'-fazom(Ni_3Al). RTG analizom je utvrđeno, da se prevlaka NiCrAlY sastoji od intermetalne ß– faze ($Ni_{1.1}Al_{0.9}$), i kubne faze (Cr_2Ni_3), a nakon intermetalnog ojačavanja, ß–faza ($Ni_{1.1}Al_{0.9}$) prelazi u □'-fazu (Ni_3Al). To znači da se i u leguri AMS 5528 i prevlaci NiCrAlY, odvijaju slični mehanizmi ojačavanja, što je važno kod izbora prevlake [2]. Granica između prevlake i legure, predstavlja mehaničku smjesu, nastalu bez difuzije i rastapanja, a proces spajanja se odvija mehaničkom aktivacijom, slično kao i kod spajanja metala eksplozijom. Utvrđeno je, da se nakon dejstva temperature, na granici spajanja nalaze aluminijev i itrijev oksid, koji imaju važnu ulogu u spriječavanju visokotemperaturne oksidacije osnovnog materijala. Za stabilnost prevlake važni su termodinamički uslovi formiranja oksidnih faza, koji zavise od aktiviteta pojedinih metala u leguri, parcijalnog pritiska kisika i afiniteta metalnih elemenata prema kisiku. Zbog razlike u afinitetu prema kisiku između elemenata u leguri, postoji tendencija da legura u procesu oksidacije bude prekrivena termodinamički najstabilnijim oksidom. Početno obrazovani nestabilni oksidi, postepeno se transformišu u termodinamički stabilne oksidne faze [3]. Osnovni cilj je formirati kontinuirani zaštitni sloj oksida sastavljen od α- faze (Al_2O_3), koji je otporan na visokotemperaturnu oksidaciju i koji se dodatno može ojačati itrijevim oksidom (Y_2O_3).

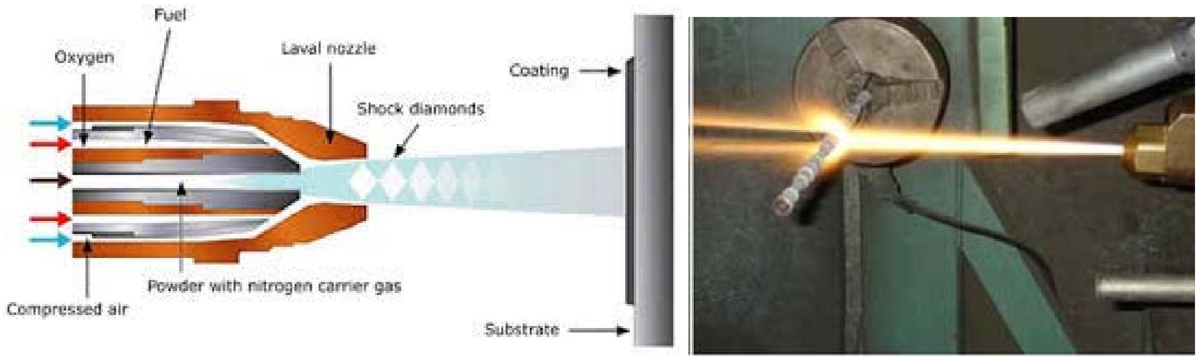
2. EKSPERIMENT

Za ispitivanje su izrađeni uzorci okruglog presjeka ϕ15 mm, od legure AMS 5528 (14.35%Cr, 25.0%Ni, 2,35%Ti, 0.10%Al). Metalna prevlaka na uzorke je nanesena postupkom Diamond Jet, pomoću detonacijskg pištolja DJ 2700. Metalni prah NiCrAlY 4516 (64.5%Ni, 24.5%Cr, 10.5%Al, 0.20%Y), doziran je u punjač praha, koji je u struji dušika uveden u plazmenu struju koja ga ogromnom brzinom baca i deponuje na uzorak. Plazmena struja se stvara uvođenjem gorivog plina (propan-butan) i kisika u komoru pištolja, gdje nastaje detonacija, koja stvara plamene i udarne talase, koji se preko mlaznica ubrzavaju do nadzvučne brzine, stvarajući u plazmenoj struji dijamantni šok. Debljina nanesene metalne prevlake iznosi 70μm. Na slici 1. prikazana je šema procesa Diamond Jet (a), i snimak proseca nanošenja prevlake na uzorak (b).

The structure of the alloy in a strengthen state is consisted of austenitic Y-base, with a separate coherent Y'-phase (Ni_3Al). X-ray analysis showed that the coating is composed of intermetallic phase ß ($Ni_{1.1}Al_{0.9}$), and the cubic phase (Cr_2Ni_3), and after the intermetallic strengthening, ß-phase ($Ni_{1.1}Al_{0.9}$) becomes Y'- phase (Ni_3Al). This means that in the alloy and in the coating NiCrAlY, similar mechanisms of strengthening are conducted, which is important in the selection of the coating [2]. The boundary between the coating and the alloy is a mechanical mixture resulted without diffusion and dissolution, and the bonding process is carried out by mechanical activation, similar to connecting metals by explosion. It was found that after the high temperatures affect, at the joint border are aluminium and yttrium oxide, which have an important role in preventing high-temperature oxidation of the base material. For the stability of the coating are important thermo-dynamic conditions of formation of oxide phases, which depend on the activity of certain metals in the alloy, the partial pressure of oxygen and affinity of metal elements to oxygen. Due to differences in affinity to oxygen between the elements in the alloy, there is a tendency that alloy during oxidation process is covered by thermodynamic-cally most stable oxide. Initial formed unstable oxides, are gradually transformed into thermo-dynamically stable oxide phases [3]. The basic aim is to form a continuous protective layer of oxide composed of phase α-(Al_2O_3), which is resistant to high temperature oxidation, and which can additionally be strengthened by yttrium oxide (Y_2O_3).

2. EXPERIMENTAL

For the carried out tests were made samples of circular section ϕ 15 mm from alloy AMS 5528 (14.35%Cr, 25.0%Ni, 2.35%Ti, 0.10%Al). The metal coating is applied to samples by Diamond Jet procedure, using detonation gun DJ 2700. Metal powder NiCrAlY 4516 (64.5%Ni, 24.5%Cr, 10.5%Al, 0.20%Y), is dosed in the charging of powder, which is, by nitrogen flow inducted in a plasma flow, which dumps it rapidly and applies it on the sample. The plasma flow is created by induction of fuel gas (propane-butane) and oxygen in the chamber of the gun, where it causes detonation, which creates a blast and shock waves that through the nozzles accelerate to supersonic speed, creating diamond shock in the plasma flow. The thickness of applied metal coating is 70μm. Figure 1 shows a diagram of the Diamond Jet procedure(a), and process of applying coating to the sample (b).



a b

Slika 1. *Šema procesa HVOF Diamond Jet (a) i proces nanošenja prevlake na uzorak (b)*
Figure 1. *Scheme of the procedure HVOF Diamond Jet and of the process of coating of the sample (b)*

Na uzorcima su izvršeni termički tretmani rastvornim žarenjem na 980ºC i precipitacionim ojačavanjem na 720ºC u trajanju od 12 sati. Kinetika oksidacije i mehanizam procesa stabilizacije mikrostrukture na povišenim temperaturama, ispitani su nakon oksidacije na zraku na temperaturi od 1000ºC u trajanju od 124 sata. Da bi se utvrdili mehanizmi koji se odvijaju u strukturi prevlake i na faznim granicama, kod dejstva visokih temperatura, ispitane su mikrostrukture na poprečnom presjeku uzoraka u ojačanom stanju (slika 2.a.b), i površini prevlake nakon oksidacije (slike 3.a.b.c i 3.a.b.c and 4.a.b.c.d). Uzorci su nagriženi u reaktivu Kalling, a izvršena su ispitivanja strukture na skenirajućem elektronskom mikroskopu Joel JSM 5610 (SEM) i RTG analiza na difraktometru Panalitical X Pert Pro.

3. RESULTATI I DISKUSIJA

Na SEM slici 2.a, vide se mikrostruktura prevlake NiCrAlY, spoj prevlaka-legura, i međufazne granice između rastopljenih i nerastopljenih čestica. Linijska EDS analiza (slika 2.b), pokazuje da u prevlaci, na međufaznim granicama, i posebno na granici prevlaka-legura, dolazi do povećanja sadržaja aluminija, itrija i kisika, pa se na osnovu toga, može zaključiti da je došlo do formiranja aluminijevog oksida (Al_2O_3) i itrijevog oksida (Y_2O_3). Prisustvo itrija, u obliku fino dispergovanih čestica itrijevog oksida (Y_2O_3), može ojačati i povećati stabilnost aluminijevog oksida (Al_2O_3). Ispitivanjem površine prevlake nakon cikličnog oksidacionog žarenja na zraku na temperaturi 1000ºC u trajanju od 124 sata, na međufaznim i faznim granicama, EDS maping i linijskom analizom, potvrđeno je još izražajnije prisustvo oksida aluminija i itrija (Slika 3.a.b.c.d).

On the samples were carried out heat treatments by solution annealing at 980ºC and precipitation strengthening at 720ºC during a period of 12 hours. Oxidation kinetics and mechanism of the stabilization process of the microstructure at elevated temperatures, were tested after oxidation in air at a temperature of 1000ºC during a period of 124 hours. In order to determine the mechanisms that take place in the structure of the coating and at the phase boundaries, at high temperature, were examined microstructures in cross-section of samples in strengthen condition (Figure 2.a.b.), and surface of coating after oxidation (Figures 3.a.b.c. and 4.a.b.c.d). The smples were etched in a reagent Kalling, and structure tests were performed by Scanning Electron Microscopy Joel JSM 5610 (SEM) and X-ray analisis bay Panalitical X-Pert Pro.

3. RESULTS AND DISCUSSION

Microstructure tests were conducted by Scanning Electron Microscopy (SEM). On SEM image (Figure 2a), we can see the microstructure of NiCrAlY coatings, joint coating -alloy, and interfacial boundaries between the molten and infusible particles. Line EDS analysis (Figure 2.b), shows increased content of aluminum, yttrium and oxygen in the coating, on the interphase boundaries, and especially on the border alloy-coating, and on that basis, it can be concluded that aluminium oxide (Al_2O_3) and yttrium oxide (Y_2O_3)are formed. The presence of yttrium, in the form of finely dispersed particles of yttrium oxide (Y_2O_3), can strengthen and increase the stability of aluminum oxide (Al_2O_3). Test of coating surface after cyclic oxidation annealing in air at a temperature of 1000ºC during a period of 124 hours, at the interphase and the phase boundaries, by EDS mapping and linear

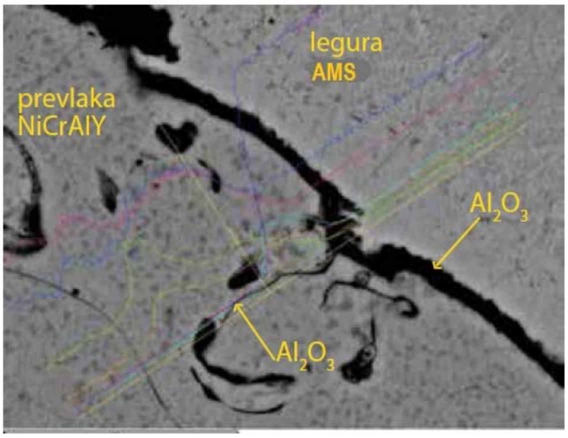
U početnoj fazi procesa oksidacije, formira se siva oksidna faza bogata sa kromom, i to pretežno na površinskom dijelu prevlake, između krhotina i pora, jer tu postoji velika reaktivna površina u koju lako prodire kisik. Ispod sive oksidne faze, na polu-rastopljenim česticama nalazi se tamna oksidna faza aluminijevog oksida, koja može biti ojačana oksidom itrija.

Prisustvo oksida kroma i nikla, osiromašuje prevlaku na sadržaj aluminija, što uzrokuje pospješenje formiranja sive oksidne faze, koja mjenja termodinamičku ravnotežu, i na taj način pospješuje difuziju aluminija prema spoju prevlaka-legura. Ispitivanjem strukture na SEM, i EDS maping i linijskom analizom potvrđeno je, da siva oksidna faza bogata sa kromom, inicira stvaranje zaštitniog sloja aluminijevog oksida ispod sive oksidne faze (Slika 4.a.b.c).

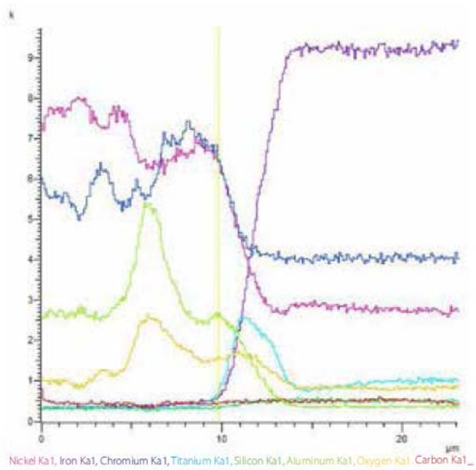
analysis, it was confirmed even more expressive presence of aluminum oxide and yttrium (Figure 3.a.b.c.d).

In the initial stage of the oxidation process, is formed a grey oxide phase rich in chromium, predominantly on the surface of the coating, between the debris and pore, because there is a large reactive surface which easily penetrates oxygen. Under the grey oxide phase, on the semi-molten particles is the dark phase of alumina oxide, which can be strengthen by yttrium oxide.

With the presence of oxides of chromium and nickel, the coating becomes poor in aluminum content, which speeds up formation of the grey oxide phases, which changes the thermodynamic equilibrium, and thus improves the diffusion of aluminum towards the joint-alloy-coating. Testing the structure by SEM and EDS mapping and line analysis confirmed that grey oxide phase rich in chromium, initiates the formation of protective aluminum oxide layer under the grey oxide phase (Figure 4.a.b.c).



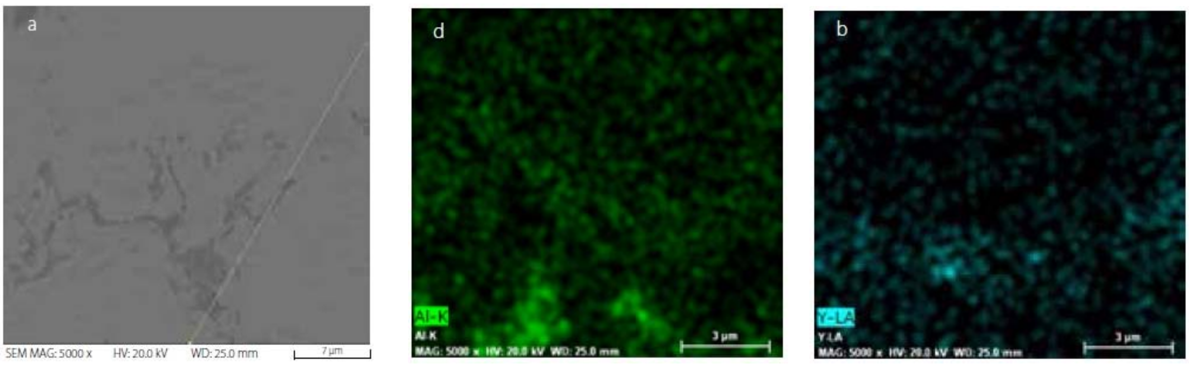
a

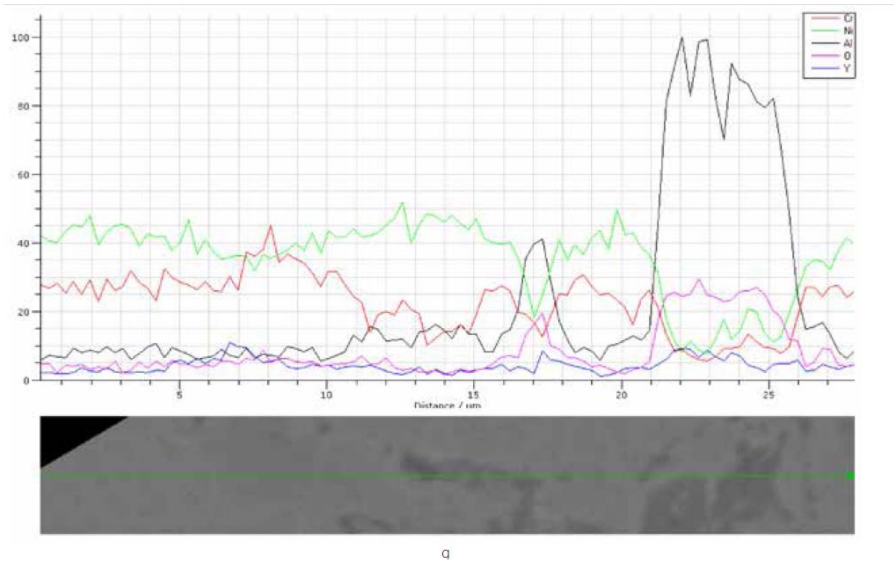


b

Slika 2. *SEM struktura prevlake i legure (a) i EDS linijska analiza (b)*

Figure 2. *SEM structure of the coating and alloy (a) and EDS line analysis (b)*

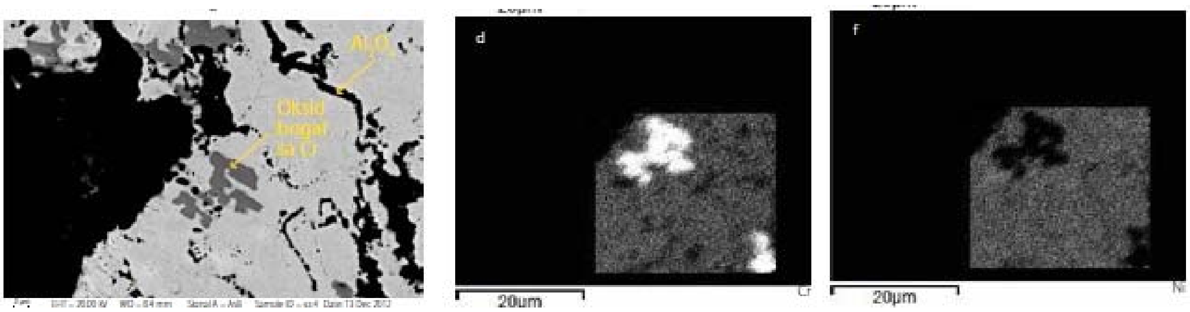




d

Slika 3. *SEM struktura površine prevlake nakon žarenja na 1000ºC od 124 sata (a), EDSmaping (b,c) i linijska analiza (d)*

Figure 3. *SEM structure of the coating surface after annealing at 1000ºC during a period of 124 hours (a), EDS mapping (b, c) and line analysis (d)*



a b c

Slika 4. *SEM struktura površine prevlake nakon žarenja na 1000ºC od 124 sata (a) i EDS maping analiza (b,c)*

Figure 4. *SEM structure of the coating surface after annealing at 1000ºC during a period of 124 hours (a) and EDS mapping analysis (b, c)*

4. ZAKLJUČAK

Za formiranje stabilnog zaštitnog sloja protiv dejstva visokih temperatura, potrebno je da se na međufaznim granicama unutar prevlake, te na sloju prevlaka-legura formira stabilni aluminijev oksid (Al_2O_3), ojačan oksidom itrija (Y_2O_3), i oksidom kroma (Cr_2O_3). Može se konstatovati, da je na osnovu ispitivanja sadržaja i raspodjele legirajućih elemenata, utvrđen mehanizam formiranja i evolucije oksida na prevlaci NiCrAlY, nakon oksidacije na temperaturi 1000ºC u trajanju od 124 sata. Polurastopljene čestice, krhotine i pore, u slabo prionljivom sloju, rezultiraju nastajanje sive oksidne mješavine i gubitkom oksidacione otpornosti ovog sloja.

4. CONCLUSION

To form a stable protective layer against the effects of high temperatures, it is necessary to form stable aluminum oxide (Al_2O_3), strengthen with yttrium oxide (Y_2O_3) and chromium oxide (Cr_2O_3) on the interphase boundaries within the coating, and on the joint coating- alloy.It can also be concluded that on the basis of test content and distribution of alloying elements, is defined mechanism for the formation and evolution of oxide on the coating NiCrAlY after oxidation at 1000ºC during a period of 124 hours. The semi-molten particles, debris and pores in uncompact layer , result in the formation of grey oxide mixture and the loss of the oxidation resistance of this layer.

Siva oksidna faza bogata sa kromom, inicira formiranje stabilnog aluminijevog oksida koji se raspoređuje po međufaznim granicama i na granici spoja prevlake i legure.

The grey oxide phase rich in chromium, initiates the formation of a stable aluminum oxide which is allocated on the interphase boundaries and on borders of the joint coating-alloys.

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